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REVIEW ARTICLE

APPLICATION OF HARD SPHERE EQUATION OF STATES FOR THE CALCULATION OF THERMODYNAMIC PROPERTIES OF LIQUIDS

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ABSTRACT

Different models for the Hard Sphere equation of states have been utilized to compute the two thermodynamic properties, isothermal compressibility (β_T) and the thermal expansion coefficient (α_P) . The pure liquids used for investigation are n-hexane, n-heptane, n- dodecane, cyclohexane and toluene. Both the properties have been calculated at varying temperatures (293.15K to 333.15K). The obtained values of isothermal compressibility and thermal expansion coefficient have been compared with the experimentally evaluated values. The results of the calculation are observed to be in satisfactory agreement with experimental findings collected from literature.

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INTRODUCTION

The thermodynamic properties of binary liquid mixtures play a significant role in understanding the nature of molecular interactions occurring in the mixtureand these properties also find applications in several industrial and technological processes. Density, the speed of sound, etc. are often used for the determination of various thermodynamic properties of binary liquid mixtures. The thermophysical characterization of liquids is very useful which can be carried out either experimentally or by thermodynamic modelling based on equations of states and statistical mechanical models. With equations of state, isothermal compressibility and thermal expansion coefficient data allows the determination of the ability of a given equation to correlate PVT data. This also allows to determine isentropic compressibilities from density and sound speed measurements. A comparative study of the applicability of various liquid state theories employed for the estimation of thermodynamic and other related properties has been done earlier by several workers[1-15]. Thermodynamic properties of liquids and liquid mixtures like isentropic compressibility, isothermal compressibility, heat capacity ratio, thermal expansivity etc. provide a lot of information about molecular interactions occurring in liquids[16, 19-25]. Tyrer[26,27] was the first investigator who recognised that the compressibility values obtained by the early workers were neither truly adiabatic nor truly isothermal. He determined the adiabatic compressibilities for a few liquids with a piezometer and with the help of the usual thermodynamic relation, he calculated the isothermal compressibility in each case. Following the Tyrer's method, Dakshinamurti[33] studied the compressibility of some essential and vegetable oils with a view to connect it with the phenomenon of light scattering. Later Bhagvantam[29], Rao, Einstein- Smoluchouski, Krishnan[43] and others studied[31-32] and gave different theories for compressibility. As the thermodynamic studies [21,33] are of great help in characterising the structure and properties of solution. Some models have been applied to estimate the values of isothermal compressibility (β_T) at varying temperatures in this work. The liquids used for investigations are n-hexane, n-heptane, n- dodecane, cyclohexane and toluene. The density and sound velocity data has been employed. For the same liquids, the thermal expansion coefficient (α) has also been computed using various models employing density and sound speed data.

THEORETICAL APPROACH

The calculation of isothermal compressibilities for five pure liquids, expressions using the seven rigid sphere equations of state are as follows:

$$PV/NkT = (1+y+y^2)/(1-y)^3 \quad (1)$$

$$PV/NkT = (1+2y+3y^2)/(1-y)^2 \quad (2)$$

$$PV/NkT = (1+y+y^2-y^3)/(1-y)^3 \quad (3)$$

$$PV/NkT = 1/(1-y)^4 \quad (4)$$

$$PV/NkT = 1/(1-y)^2 \quad (5)$$

$$PV/NkT = (1+y^2/8)/(1-y)^2 \quad (6)$$

$$PV/NkT = (1+4y + 10y^2 + 18.36 y^3 + 28.2 y^4 + 39.5 y^4+.) \quad (7)$$

Where P, V, T, N and k are respectively the pressure, volume, absolute temperature, Avogadro's number and Boltzmann constant,

$y = \pi a^3 N/ 6 V$

Packing fraction and a is the hard sphere diameter of the molecule[34]. The expressions [29,18-19] for the isothermal compressibility β_T, corresponding to eq.s 1-7 are as [34]:

$$\beta_T= (V/RT) (1-y)^4/(1+2y)^2 \quad (8)$$

$$\beta_T= (V/RT) (1-y)^3/(1+5y+9y^2-3y^3) \quad (9)$$

$$\beta_T= (V/RT) (1-y)^4/(1+4y+4y^2-4y^3+y^4) \quad (10)$$

$$\beta_T= (V/RT) (1-y)^5/(1+3y) \quad (11)$$

$$\beta_T= (V/RT) (1-y)^3/(1+y) \quad (12)$$

$$\beta_T=(V/RT)8(1-y)^3]/(8+8y+3y^2-y^3) \quad (13)$$

$$\beta_T= (V/RT)(1+8y+30y^2+73.44y^3+141y^4+273y^5)^{-1} \quad (14)$$

Thermal expansion coefficient (α) has been evaluated using seven hard sphere models[34]. Their generalized expression for the thermal expansion coefficient is

$$\alpha= (1/T) [a b /\{b. y(da/dy)_T - n ay(db /dy)_T+ a b\}] \quad (15)$$

Where a and b are the function of packing fraction y, n is an integer. Thiele- Lebowitz model:

Putting $a= 1+y+y^2$, $b= 1-y$ and $n=3$ in eq. (11), we get

$$\alpha = (1-y^3)/T. (1-2y)^2 \quad (16)$$

Thiele model:

Putting $a= 1+2y+3y^2$, $b= 1-y$, $n= 2$, we get

$$\alpha = (1+2y+3y^2) (1-y)/T (1+5y+9y^2-3y^3) \quad (17)$$

Carnhan – Starling model:

Putting $a= 1+y+y^2-y^3$, $b=1-y$ and $n=3$, we get

$$\alpha = (1+y+y^2-3y^3) (1-y) /T (1+4y+4y^2-4y^3+y^4) \quad (18)$$

Guggenheim model:

Putting $a= 1$, $b= (1-y)$ and $n= 4$, we get

$$\alpha = (1-y) /T (1+3y) \quad (19)$$

Scaled – particle theory model:

Putting $a=1$, $b= (1-y)$ and $n= 2$, we get

$$\alpha = (1-y) / T (1+y) \quad (20)$$

Henderson model:

Putting $a= 1+y^2/8$, $b= 1-y$ and $n=2$, we get

$$\alpha = (8+y^2) (1-y) / (8+8y+3y^2-y^3) \quad (21)$$

Hoover – Ree model:

Putting $a= 1+4y + 10 y^2 + 18.36 y^3 + 28.2 y^4 + 39.5y^5 +...$

$b= 1$ and $n=1$, we get

$$\alpha = (1+4y + 10y^2 + 18.36 y^3 + 28.2y^4 + 39.5y^5) / T (1+8y + 30y^2+ 73.44 y^3+ 141y^4 +237y^5) \quad (22)$$

RESULTS AND DISCUSSION

All the parameters of the pure components needed for the calculation of isothermal compressibility (β_T) and thermal expansion coefficient (α) have been taken from the literature[38] and given in table 1.1.

Table 1.1: Density (ρ), Molar mass (M), Molar Volume (V_m), Ultrasonic velocity (u), Van der Waal Constant (b) of pure components at different temperatures

T(K)	Liquid	ρ (g cm^{-3})	M (g/mol)	V_m (cm^3/mol)	u (cms^{-1})	b (cc/mol)
293.15	n-Hexane	0.6591	86.2	130.722919	107600	175.3
	n-Heptane	0.68369	100.2	146.5576504	113100	203.8
	n-Dodecane	0.74875	170	227.0450751	130120	374.1
	Cyclohexane	0.77853	84	107.8956495	125300	141.3
	Toluene	0.86684	92	106.1326196	130400	149.9
298.15	n-Hexane	0.65489	86.2	131.6251584	105620	175.3
	n-Heptane	0.6796	100.2	147.4396704	112850	203.8
	n-Dodecane	0.74518	170	228.1328001	128090	374.1
	Cyclohexane	0.77387	84	108.5453629	125780	141.3
	Toluene	0.8622	92	106.703781	130290	149.9
313.15	n-Hexane	0.6411	86.2	134.4564031	99239	175.3
	n-Heptane	0.66674	100.2	150.2834688	106670	203.8
	n-Dodecane	0.7344	170	231.4814815	122190	374.1
	Cyclohexane	0.75971	84	110.5685064	116890	141.3
	Toluene	0.8482	92	108.4649847	123980	149.9
333.15	n-Hexane	0.62212	86.2	138.5584775	90856	175.3
	n-Heptane	0.6491	100.2	154.3675859	98592	203.8
	n-Dodecane	0.7199	170	236.1439089	114660	374.1
	Cyclohexane	0.7404	84	113.452188	107030	141.3
	Toluene	0.8292	92	110.9503136	115800	149.9

Table 1.2 Isothermal compressibility ($\beta_T * 10^{12}$) for five pure liquids at varying temperatures.

	T (K)	β_T (LFH) Dyne^{-1} cm^2	β_T (Thick) Dyne^{-1} cm^2	β_T (C-S)Dyne^{-1} cm^2	β_T (G) Dyne^{-1} cm^2	β_T (F) Dyne^{-1} cm^2	β_T (H)Dyne^{-1} cm^2	β_T (H-R) Dyne^{-1} cm^2	β_T (lit.) Dyne^{-1} cm^2
n-hexane	293.15	375.38	440.82	394.92	347.172	118.01	114.79	420.47	1613
	298.15	385.34	451.38	405.09	356.87	120.27	117.03	430.40	1672
	313.15	417.43	485.32	437.85	388.20	127.44	124.12	462.37	1977
	333.15	466.17	536.56	487.49	435.89	138.06	134.62	510.84	
n-heptane	293.15	379.00	451.28	400.37	347.82	123.89	120.32	431.50	1371
	298.15	388.06	461.99	409.67	356.61	126.03	122.43	440.57	1440
	313.15	418.04	492.96	440.35	385.73	133.00	129.31	470.51	1666
	333.15	436.038	540.70	486.32	429.57	143.21	139.40	515.37	2027
n-dodecane	293.15	335.009	432.92	362.32	293.11	134.21	129.18	427.08	
	298.15	342.60	441.53	370.25	300.26	136.39	131.33	434.92	987
	313.15	366.58	468.57	395.26	322.86	143.21	138.01	459.59	
	333.15	401.45	507.61	431.53	355.86	152.91	147.52	495.29	1251
cyclohexane	293.15	330.92	385.33	347.26	307.48	101.49	988.31	367.16	
	298.15	338.41	393.23	354.90	314.80	103.15	100.47	374.62	1120
	313.15	362.26	418.33	379.20	338.13	108.37	105.63	398.35	
	333.15	397.61	455.37	415.16	372.79	115.94	113.13	433.48	1520
Toluene	293.15	262.02	313.96	277.31	239.61	871.41	845.63	300.61	
	298.15	267.707	320.07	283.15	245.11	885.03	859.07	306.31	912
	313.15	285.63	339.28	302.52	262.49	927.49	900.16	324.25	
	333.15	311.93	367.32	328.44	288.05	968.48	961.21	350.51	

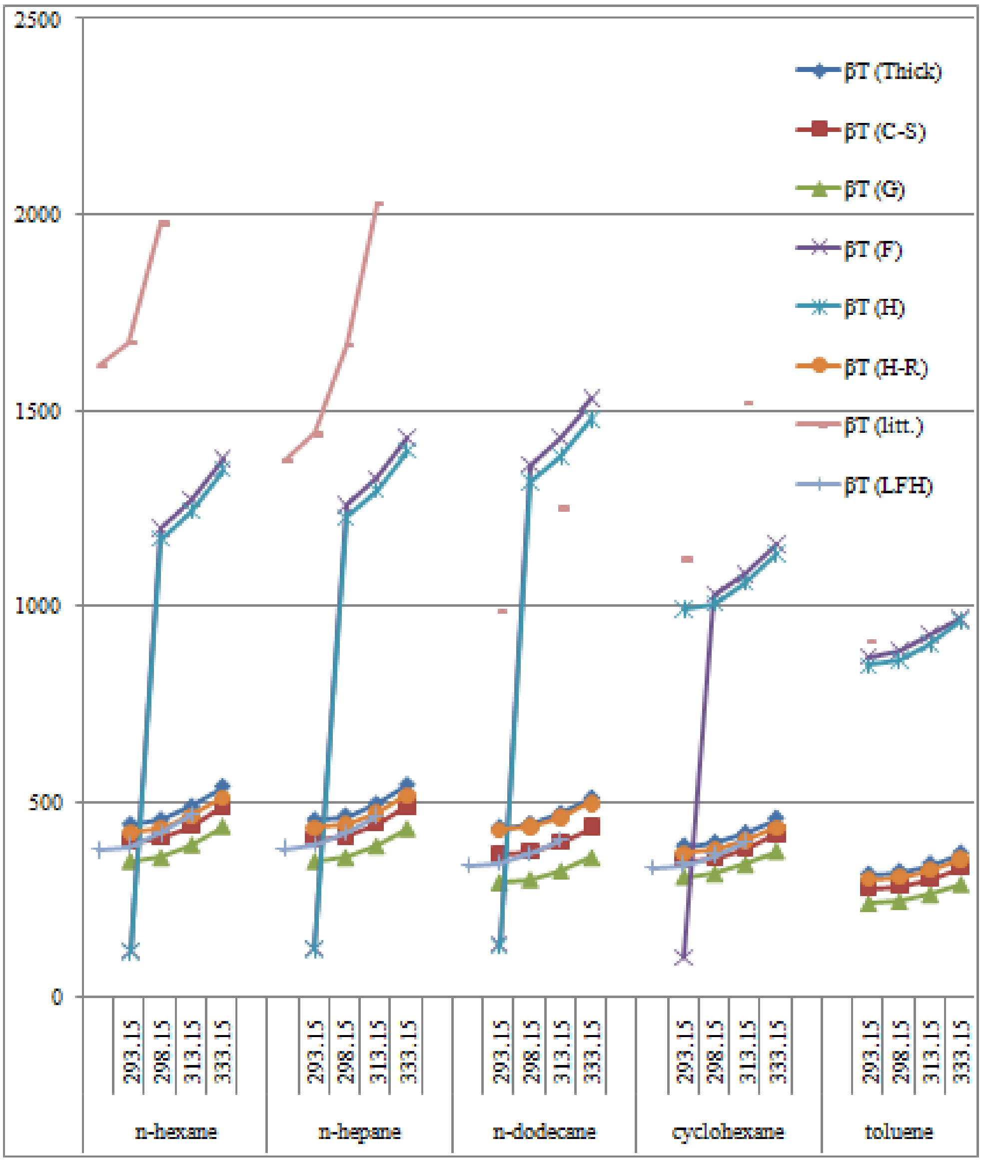

Fig 1.1. Comparison of Isothermal compressibility (β_T) of various liquids at varying temperatures

Table1.3. Thermal expansion coefficient ($\alpha*10^3$) for five pure liquids at varying temperatures

Liquid	T (K)	α (T-L) K^{-1}	α (T) K^{-1}	α (C-S) K^{-1}	α (G) K^{-1}	α (S-P-T) K^{-1}	α (H) K^{-1}	α (H-R) K^{-1}	α (lit) K^{-1}
n-hexane	293.15	30.23	1.27	1.14	1.13	1.69	1.67	1.26	1.36
	298.15	28.93	1.25	1.12	1.11	1.67	1.65	1.25	1.39
	313.15	25.43	1.21	1.09	1.08	1.62	1.60	1.21	1.45
	333.15	21.53	1.17	1.06	1.05	1.56	1.53	1.15	1.56
n-heptane	293.15	35.19	1.23	1.09	1.08	1.65	1.62	1.23	1.23
	298.15	33.70	1.22	1.08	1.07	1.63	1.61	1.22	1.23
	313.15	29.60	1.18	1.05	1.04	1.57	1.55	1.17	1.29
	333.15	25.04	1.13	1.02	1.01	1.51	1.49	1.12	
n-dodecane	293.15	102.24	1.06	0.895	0.897	1.42	1.39	1.10	
	298.15	96.29	1.05	0.885	0.887	1.40	1.37	1.08	0.974
	313.15	80.95	1.01	0.859	0.860	1.35	1.33	1.04	
	333.15	65.13	0.97	0.829	0.828	1.29	1.27	0.99	
cyclohexane	293.15	27.62	1.29	1.16	1.15	1.72	1.70	1.28	
	298.15	26.56	1.28	1.15	1.14	1.71	1.68	1.27	1.22
	313.15	23.70	1.23	1.12	1.11	1.64	1.62	1.22	
	333.15	20.45	1.18	1.08	1.06	1.57	1.57	1.17	
Toluene	293.15	37.77	1.22	1.07	1.07	1.63	1.60	1.22	
	298.15	36.23	1.20	1.06	1.05	1.61	1.58	1.21	1.083
	313.15	32.06	1.16	1.03	1.02	1.55	1.53	1.16	
	333.15	27.41	1.11	0.996	0.987	1.48	1.46	1.11	

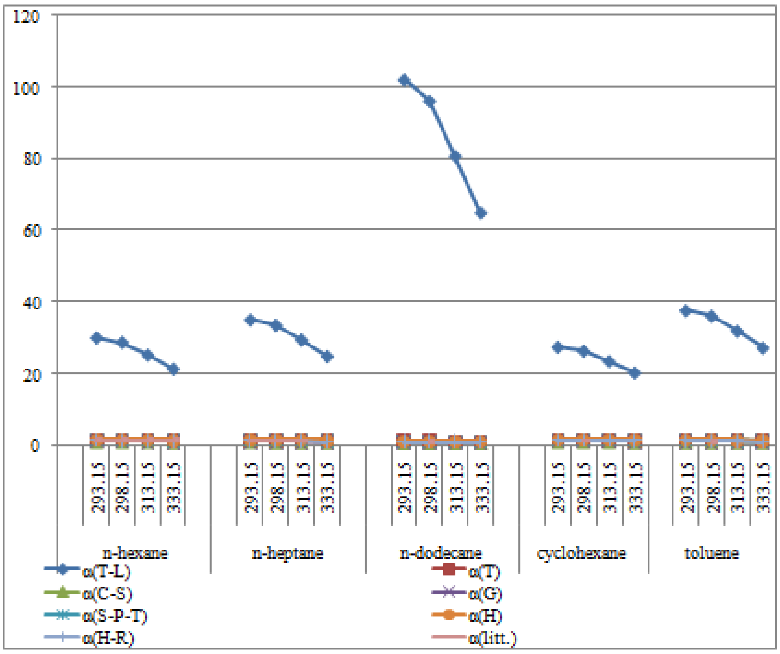

Fig 1.2. Comparison of thermal expansion coefficient (α) of various liquids at varying temperatures

The literature values of isothermal compressibility (β_T) [58] and thermal expansion coefficient (α)[38] have been listed in the last column of Table 1.2-1.3 respectively.

CONCLUSION

The results obtained for isothermal compressibility (β_T) and the thermal expansion coefficient (α_P) by applying various models to the pure liquids at different temperature are remarkable.

In all the cases of isothermal expansivity and isobaric isothermal expansivity, values obtained using different models increase with the increase in temperature values. All approaches give values which are in good agreement with literature values of α_P. From graphical representation of both the properties give satisfactory result as all models show similar trend.

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